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(54) Title: METAL TREATMENT

(57) Abstract

An acidic aqueous coating solution to be applied to galvanized metals to increase their resistance to corrosion which contains from 0.1 to 10 g/l, based on fluoride content, of a fluoride-containing compound, and from 0.015 to 6 g/l, based on metal content, of a salt of cobalt, copper, iron, manganese, nickel, strontium or zinc. Optionally, a sequestrant and/or a polymer of a (meth)acrylic acid or ester thereof can also be present. The invention also relates to concentrates for preparing the coating solutions and to processes for using the coating solutions.

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# METAL TREATMENT

This application is a continuation-in-part of application Serial No. 607,075 filed May 4, 1984 in favor of the same inventors.

This invention relates to the treatment of metals, and more particularly to the treatment of the zinc-surface of galvanized iron, galvanized steel, and the like to increase the resistance to corrosion of these metals.

## BACKGROUND OF THE INVENTION

It is known to coat zinc surfaces of galvanized metals with aqueous coating solutions that are effective in providing corrosion resistant coatings which protect the surfaces of these galvanized metals from corrosive degradation stemming from contact with the atmosphere. Besides serving to prevent or inhibit corrosion such coatings should also possess good

adherence to siccative coatings, such as paints, lacquers and the like, which may be subsequently applied to the metal for decorative or other purposes.

Two types of compositions useful for this purpose are (i) acidic compositions and (ii) alkaline compositions.

Acidic compositions, which form phosphate or chromate coatings on the zinc, are described in U.S. patent No. 3,297,494. Alkaline coatings are widely used and examples of such coatings are disclosed in U.S. patents Nos. 3,444,007; 3,515,600 and 4,278,477.

The use of chromate, phosphate or fluoride solutions to protect aluminum surfaces is disclosed in U.S. patents Nos. 2,438,877; 2,928,763; 3,377,212; 3,682,713; 3,912,548; and 4,191,596. The fluorides in these coating compositions are usually in the form of complex fluorides such as $H_2ZrF_6$, $H_2TiF_6$, and $H_2SiF_6$. These acidic coating compositions have been tried on galvanized metals but did not function as desired. The coatings after application to the galvanized metal were not readily visible as compared with the appearance of untreated metal, making it difficult to tell whether a coating had been applied.

## DESCRIPTION OF THE INVENTION

It is an object of this invention to provide an acidic coating composition to be applied to a metal surface to increase the resistance of corrosion of the metal.

It is another object of this invention to provide an acidic composition for coating metals which composition will have good adherence to a subsequently applied siccative coating.

It is a further object of this invention to provide

an acidic composition for coating metals which composition will have good adherence to a subsequently applied siccative coating.

It is a further object of this invention to provide an acidic composition for coating metals so that said coating will be visible.

It is still another object of this invention to provide a process for coating the metal to increase its resistance to corrosion.

Other objects will appear from the description which follows.

Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about".

In accordance with this invention there is provided an aqueous coating solution for metals, such as galvanized iron and steel, aluminum, and ferrous metals such as steel, which contains:

(a) from 0.1 to 10 g/l preferably from 0.1 to 2.0 g/l, based on fluoride content, of a fluoride containing compound which is either
  (i) a fluorometallic acid such as $HBF_4$, $H_2SiF_6$, $H_2TiF_6$, and $H_2ZrF_6$ or an ammonium or alkali metal salt thereof;
  (ii) hydrofluoric acid or a salt thereof; or
  (iii) a mixture of (i) and (ii);

(b) from 0.015 to 6 g/l, preferably from 0.1 to 1.0 g/l, based on metal content, of a salt or a metal such as cobalt, copper, iron, manganese, nickel, strontium, and zinc, or a mixture of two or more of the foregoing; and, optionally,

(c) a sequestrant in an amount of from a 1:1 molar

ratio to a 3:1 molar ratio of sequestrant to metal content of (b); and/or

(d) from 0.1 to 3.0 g/l, preferably from 0.1 to 1 g/l, of a polymer of acrylic acid, methacrylic acid, or an ester thereof with a $C_1$ to $C_8$ alkanol.

With respect to component (a)(i) above, $H_2TiF_6$ is the preferred fluorometallic acid and is commonly used as a 60% aqeous solution in the preparation of the compositions of this invention, and is preferably used in a quantity equal to about 1.4 g/liter of fluoride.

Concerning component (a)(ii), the salt of hydrofluoric acid can be an ammonium or alkali metal salt, or a fluoride of a metal of component (b) provided the ranges for fluoride or metal are not exceeded.

Component (a)(iii) can be a mixture of (i) and (ii) in any proportion.

With respect to component (b) the preferred salts of cobalt, copper, iron, manganese, nickel, strontium and zinc in addition to the fluoride salts, are their carbonates and bicarbonates. This serves to avoid the introduction of anions other than fluoride into the coating composition. Commercial grade nickel carbonate, which contains a minimum of about 45% nickel, is preferred. However, any salt of these metals may be used provided the anion which is introduced is not detrimental to the stability of the formulations and to the coating. Such acceptable anions include sulfate and chloride.

While the sequestrant (c) is an optional ingredient, it is beneficial to have this component present since the presence of a sequestrant extends the useful pH range of the aqueous coating solution from 2 to 5, preferably about 4, without the sequestrant, to from 2

to 7 with the sequestrant. Sequestrants that can be employed herein include the following compounds, seqestrant-active derivatives thereof, or alkali metal or ammonium salts thereof: nitrilotriacetic acid (NTA), ethylenediamine tetraacetic acid (EDTA), gluconic acid, and citric acid. In addition, the above sequestrants improve the adhesion of organic coatings applied to the coated metal substrates produced by the coating solutions of the invention.

Concerning component (d) above, a preferred polymer is ACRYSOL A-1, a 25% aqueous solution of a water-soluble polyacrylic acid having a molecular weight of up to about 500,000 (available from Rohm and Haas Co.).

In practicing the invention, it is preferred to use prior prepared concentrated aqueous solutions of the above ingredients, which are added to water in an amount to provide a coating solution of the desired composition and concentration. The concentrated aqueous solutions contain component (a) in a concentration of at least about 1 g/l, preferably from about 1 to about 15 g/l based on fluoride content, with the quantities of the other components increased proportionally so that dilution with water will give the aqueous coating solution compositions disclosed above. Preferably, the concentrate contains the desired ingredients in sufficient amounts so that a ten-fold dilution by volume of the concentrate will provide an aqueous coating solution having the desired composition and concentration. However, concentrates containing the above ingredients up to their solubility limits in water can also be used herein. Although tap water can be used in preparing the concentrate and the coating solution, it is preferred to use deionized water to avoid any possible interference from undesirable ions.

The concentrates can be formulated as described above, or quantities of bases such as NaOH, $NH_4OH$, $(NH_4)_2CO_3$, or $Na_2CO_3$ or an acid such as $H_2SO_4$ can be added so that upon dilution the correct pH is obtained for the coating solutions.

The coating solution can be applied by brushing, spraying, dipping, roll-coating and the like, with spraying or dipping being preferred. In carrying out the process of this invention the metal is preferably first cleaned, using an alkaline cleaner such as RIDOLINE 1089, which is composed of sodium carbonate, sodium hydroxide, sodium polyphosphate, and surfactants and is available from Amchem Products, Inc. of Ambler, Pa. The cleaned metal is then rinsed with water and sprayed with or dipped into the coating solution of the invention which is kept at 60°F to 160°F, preferably from 110°F to 140°F, for 1 to 300, preferably from 5 to 30 seconds. The coated metals are then rinsed with water. Preferably, a final rinse, such as a final chrome rinse with DEOXYLYTE 41, an aqueous solution containing chromic acid and formaldehyde (available from Amchem Products, Inc..), is then used. A siccative coating can thereafter be applied to the metal.

As the coating solution is used, the ingredients therein decrease in concentration and it becomes necessary to replace them. Although it is always possible to prepare a fresh solution, this is wasteful of materials present in the solution which can still be used , and is also time consuming. In practice, it is desirable to use a replenishing concentrate, and the concentrates disclosed above for use in forming the aqueous coating solutions of the invention can also be used as replenishing concentrates.

The invention will become clearer from the examples which follow. The examples are given only by

way of illustration and are not to be considered as limiting.

Examples 1 to 10 illustrate concentrate compositions according to this invention. In preparing these concentrates the desired amounts of the ingredients were dissolved in water and additional water added to bring the concentrate to the desired volume.

EXAMPLE 1

| | | |
|---|---|---|
| $H_2TiF_6$ (60% aqueous) | | 34.2 g |
| $NiCO_3$ (45% Ni) | | 4.1 g |
| Water | q.s. | 1 liter |

EXAMPLE 2

| | | |
|---|---|---|
| $H_2TiF_6$ (60% aqueous) | | 34.2 g |
| $NiCO_3$ (45% Ni) | | 8.2 g |
| Water | q.s. | 1 liter |

EXAMPLE 3

| | | |
|---|---|---|
| $H_2TiF_6$ (60% aqueous) | | 68.4 g |
| $NiCO_3$ (45% Ni) | | 8.2 g |
| Water | q.s. | 1 liter |

EXAMPLE 4

| | | |
|---|---|---|
| $H_2TiF_6$ (60% aqueous) | | 34.2 g |
| $NiCO_3$ (45% Ni) | | 14.9 g |
| Water | q.s. | 1 liter |

EXAMPLE 5

| | | |
|---|---|---|
| $H_2TiF_6$ (60% aqueous) | | 34.2 g |
| $NiCO_3$ (45% Ni) | | 4.1 g |
| Acrysol A-1 | | 40.0 g |
| Water | q.s. | 1 liter |

EXAMPLE 6

| | | |
|---|---|---|
| $H_2ZrF_6$ | | 26.1 g |
| $CaCl_2$ | | 3.6 g |
| Water | q.s. | 1 liter |

EXAMPLE 7

| | | |
|---|---|---|
| $H_2TiF_6$ (60% aqueous) | | 34.2 g |
| $CoCO_3$ | | 3.8 g |
| Water | q.s. | 1 liter |

EXAMPLE 8

| | | |
|---|---|---|
| $H_2TiF_6$ (60% aqueous) | | 34.2 g |
| $CoCO_3$ | | 9.3 g |
| Acrysol A-1 | | 40.0 g |
| Water | q.s. | 1 liter |

EXAMPLE 9

| | | |
|---|---|---|
| $H_2TiF_6$ (60% aqueous) | | 34.2 g |
| $CuSO_4 \cdot 5H_2O$ | | 10.0 g |
| Water | q.s. | 1 liter |

EXAMPLE 10

| | | |
|---|---|---|
| $H_2TiF_6$ (60% aqueous) | | 34.2 g |
| $MnCO_3$ | | 3.68 g |
| Water | q.s. | 1 liter |

Examples 11 through 12 illustrate coating solutions prepared from various concentrates and the processes of treating galvanized metals with these coating solutions.

EXAMPLE 11

A. Preparation of the coating solution

A coating solution was prepared by diluting 10 liters of the concentrate of Example 1 to 100 liters with deionized water. The pH of the solutions was

adjusted to about 4.0 by the addition of ammonium hydroxide.

B. Coating Process

Armo G-60 and G-90 hot dipped galvanized steel panels were first cleaned by spraying for 15 sec. with an aqueous solution (1 oz/gal) of RIDOLINE 1089 at about 130°F. The panels were then rinsed with water and then immersed in the coating solution, prepared as described above, for 15 seconds at a temperature of about 130°F. The coated panels were then rinsed in water and dried. The protective coating was dark in color. The coated panels were very resistant to corrosion and the protective coatings thereon possessed good adherence to subsequently applied siccative coatings such as polyester, polyester melamines, siliconized polyesters, fluorocarbons, and the like using epoxy or acrylic primers.

EXAMPLE 12

The procedure of Example 11 was repeated using the concentrate of Example 5.

The coating was somewhat lighter in color than the coating of Example 11. This is apparently due to the presence of the acrylic polymer. The coating provided good protection against corrosion and possessed good adhesion to subsequently applied siccative coatings.

Following the procedures of Examples 11 and 12 using the concentrates of Examples 2 to 4 and 6 to 10, similar dark coatings, providing good resistance to corrosion and having good adhesion to applied siccative coatings, were obtained.

As the galvanized metals were continued to be processed through the coating solution, the pH thereof slowly rose and the coating took on a lighter (bluish) appearance. The adhesion to subsequently applied siccative coatings was also reduced, although the corro-

sion resistance was still good. These results indicate that either the coating solution should be replaced or the ingredients therein be replenished. As discussed above, replacement of the solution is time-consuming and wasteful of materials. A suitable replenisher concentrate is set forth in Example 13.

EXAMPLE 13

| | | |
|---|---|---|
| $H_2TiF_6$ (60% aqueous) | | 107.20 g |
| $NiCO_3$ (45% Ni) | | 51.20 g |
| Sulfuric acid, 66° Be | | 458.00 g |
| Deionized water | q.s. | 1 liter |

The replenisher concentrate is added until the pH of the bath is brought into the operating range given above.

Replenisher concentrates for coating solutions containing other ingredients may be prepared by having in the replenisher concentrate the same fluorometallic acid and the same metallic ion which are present in the coating solution.

EXAMPLE 14

A. Preparation of the coating solution

A coating solution was prepared by adding the following ingredients to deionized water:

2.0 g/l $H_2TiF_6$
0.4 g/l $NiCO_3$
0.6 g/l citric acid

The pH of the solution was adjusted to 6.0 by the addition of ammonium carbonate.

B. Coating process

Armo G-60 and G-90 hot dipped galvanized steel panels were first cleaned by spraying for 15 sec. with an aqueous solution (1 oz/gal) of RIDOLINE 1089 at about 130°F. The panels were then rinsed with water

and then immersed in the coating solution, prepared as described above, for 7 seconds at a temperatre of about 130°F. The coated panels were then rinsed in water and dried. The protective coating was dark in color. The coated panels were very resistant to corrosion and the protective coatings thereon possessed good aherence to subsequently applied siccative coatings such as polyesters, polyester melamines, siliconized polyesters, fluorocarbons, and the like using epoxy or acrylic primers.

EXAMPLE 15

The process of Example 14 was carried out except that in A. 4.2 g/l of disodium EDTA was used instead of 0.6 g/l of citric acid, and B. the treatment time was 15 seconds. The same results were obtained.

EXAMPLE 16

The process of Example 14 was carried out except that in A. 4.9 g/l of gluconic acid was present in place of 0.6 g/l of citric acid. The same results were obtained.

EXAMPLE 17

A. Preparation of the coating solution

A coating solution was prepared by adding the following ingredients to deionized water:

0.515 g/l $NiF_2 \cdot 4H_2O$

0.688 g/l $H_2SO_4$ (66 Be°)

The pH of the solution was adjusted to 3.75 by the addition of ammonium carbonate.

B. Coating process

Armo G-60 and G-90 hot dipped galvanized steel panels were first cleaned by spraying for 15 sec. with an aqueous solution (1 oz/gal) of RIDOLINE 1089 at

about 130°F. The panels were then rinsed with water and then immersed in the coating solution, prepared as described above, for 15 seconds at a temperature of about 130°F. The coated panels were then rinsed in water and dried. The protective coating was dark in color. The coated panels were very resistant to corrosion and the protective coatings thereon possessed good adherence to subsequently applied siccative coatings such as polyesters, polyester melamines, siliconized polyesters, fluorocarbons, and the like using epoxy or acrylic primers.

## CLAIMS

1. An aqueous solution for coating the surface of a metal consisting essentially of:
(a) from about 0.1 to about 10 g/l, based on fluoride content, of a fluoride-containing compound which is either
(i) the fluorometallic acid $HBF_4$, $H_2SiF_6$, $H_2TiF_6$ or $H_2ZrF_6$, or an ammonium or alkali metal salt thereof,
(ii) hydrofluoric acid or a salt thereof, or
(iii) a mixture of (i) and (ii);
(b) from about 0.015 to about 6 g/l, based on metal content, of a salt of cobalt, copper, iron, manganese, nickel, strontium, zinc, or a mixture of two or more thereof; and, optionally, one or both of the following:
(c) a sequestrant which is one or more of nitrilotriacetic acid, ethylenediamine tetraacetic acid, gluconic acid, citric acid, a sequestrant-active derivative of the foregoing, and an alkali metal or ammonium salt of the foregoing, wherein the sequestrant is present in from about a 1:1 molar ratio to about a 3:1 molar ratio of sequestrant to metal content of (b); and
(d) from 0 to about 3.0 g per liter of a polymer which is polyacrylic acid, polymethacrylic acid, or a $C_1$ to $C_8$ alkanol ester of either of the foregoing.

2. An aqueous solution in accordance with Claim 1 wherein the pH of the solution is from about 2 to above 5 when component (c) is not present, and from about 2 to about 7 when component (c) is present.

3. An aqueous solution in accordance with Claim 1 wherein the pH of the solution is about 4.

4. An aqueous solution in accordance with Claim 1 wherein

component (a) is present in from about 0.1 to about 2.0 g/l, based on fluoride content.

5. An aqueous solution in accordance with Claim 1 wherein component (b) is present in from about 0.1 to 1.0 g/l, based on metal content.

6. An aqueous solution in accordance with Claim 1 wherein the fluorometallic acid in (a)(i) is $H_2TiF_6$.

7. An aqueous solution in accordance with Claim 1 wherein the salt of the metal in component (b) is a salt of nickel.

8. An aqueous solution in accordance with Claim 7 wherein the salt of nickel is nickel carbonate.

9. An aqueous solution according to Claim 6 wherein the salt of the metal in component (b) is a salt of nickel.

10. An aqueous solution according to Claim 1 wherein component (d) is about 1 g/liter of a polyacrylic acid.

11. An aqueous concentate for the preparation of the aqueous solution of Claim 1 which contains the components of Claim 1 in the same ratios as set forth therein except for having less water content.

12. A process for providing a coating on a galvanized metal, said coating having increased resistance to corrosion and having good adherence to a subsequently applied siccative coating, which process comprises:
(A) cleaning the galvanized metal to be coated,
(B) rinsing the galvanized metal, and
(C) applying thereto the coating solution according to Claim 1.

13. A process for providing a coating according to Claim 12 wherein the coating is applied by dipping the metal in the solution for a period of time of from about 1 to about 300 sec at a temperature from about 60 to about 160°F.

14. A process for providing a coating according to Claim 12 wherein the period of time is from about 5 to about 30 sec at a temperature from about 110 to about 140°F.

15. A process for providing a coating according to Claim 12 wherein in step (C) the coating solution is applied by spraying or dipping.

16. A galvanized metal having a corrosion resistant coating prepared by the process of Claim 12.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US85/00797

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL.3 C23F 7/00 C23F 9/00
U.S. CL. 148 6.14R, 31.5

## II. FIELDS SEARCHED

Minimum Documentation Searched [4]

| Classification System | Classification Symbols |
|---|---|
| U.S. | U.S. 148/6.14R, 31.5 |

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

## III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

| Category * | Citation of Document, [16] with indication, where appropriate, of the relevant passages [17] | Relevant to Claim No. [18] |
|---|---|---|
| A | US, A, 4,294,627, PUBLISHED 13 OCTOBER 1981 HEYES | |
| Y | US, A, 3,396,650, PUBLISHED 29 JUNE 1976 BINNS | 1-16 |
| Y | US, A, 4,422,886, PUBLISHED 27 DECEMBER 1983 DAS | 1-16 |
| Y | US, A, 1,710,743, PUBLISHED 30 APRIL 1929 PACZ | 1-16 |
| Y | US, A, 4,370,177, PUBLISHED 25 JANUARY 1983 FRELIN | 1-16 |
| Y | US, A, 3,539,403, PUBLISHED 10 NOVEMBER 1970 RIES | 1-16 |
| A | US, A, 4,273,592, PUBLISHED 16 JUNE 1981 KELLY | |
| A | US, A, 4,277,292, PUBLISHED 07 July 1981 | |

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## IV. CERTIFICATION

| Date of the Actual Completion of the International Search [9] | Date of Mailing of this International Search Report [9] |
|---|---|
| 13 JUNE 1985 | 03 JUL 1985 |
| **International Searching Authority [1]** | **Signature of Authorized Officer [10]** |
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